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ABSORPTION BY COLLOIDAL AND NONCOLLOIDAL SOIL CONSTITUENTS.

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CONTENTS.

INTRODUCTION.

Absorption[1] by soils has been investigated since the early days of soil science. Nevertheless, the parts played by the different soil constituents in absorption phenomena have not been accurately determined. It has been recognized in a general way that the finer soil particles are more absorptive than the larger particles and that organic constituents are among the most highly absorptive. However, very few accurate quantitative data have been obtained on the absorptive capacities of soil particles of different sizes.

A soil is of course a very intimate mixture of many components, and it would seem at first thought unreasonable to allocate such a general property as absorption to any one class of constituents. However, in 1909, Ashley (2)[2] proposed the absorption of malachite green as a measure of the relative colloidal contents of ceramic clays. This was equivalent to assuming that practically all the absorption of the clay was due to colloids and that the colloids in different clays

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[1] The term "absorption" is used in this paper in the general sense, for which "sorption" has recently been proposed. It is not intended to convey any idea of the mechanism of the process as is done by the term "adsorption" or by "absorption" used in a more specific sense.

[2] Reference is made by number (italic) to "Literature Cited," p. 19.

had similar absorptive capacities.   In 1912 Mitscherlich (16, p. 476) made a general statement that the hygroscopicity of noncolloidal soil particles was almost nothing, but that the colloids in different soils must have different capacities for absorbing water vapor.   Evidence recently accumulated 'in this laboratory also seems to show that practically all the absorptive capacity of the soil is located in the colloidal material.   For instance, samples of the colloidal matter, or "ultra clays,"[3] extracted from a large number of different soils by use of a high-power centrifuge,[4] show absorptive capacities for malachite green, ammonia gas, and water vapor which are two to twenty times higher than those of the original soils.

Moore, Fry, and Middleton, (17) of this bureau, have suggested that the colloidal content of the soil may be measured by comparing the absorptive power of the soil for malachite green or ammonia gas with the absorptive power of the mixed colloids, or ultra clay, extracted from the soil, if soil absorption is due almost entirely to the colloids.   While the various ultra clays absorb widely different amounts of malachite green and of ammonia gas, they have a much more constant absorptive capacity for water vapor.   It was, therefore, suggested by Robinson (21) that the colloidal content of the soil might be estimated by dividing its water-absorption value by a factor which is an average of the specific absorptions of a large number of different ultra clays, if the noncolloidal particles do not absorb appreciably.   This latter method would obviate the necessity of extracting a sample of colloid from the soil.

Although there is considerable evidence that by far the greater part of the soil's absorptive capacity is due to colloids, it is obviously important to obtain quantitative data on the relative absorptions of the colloidal and noncolloidal constituents, if absorptive methods are to be used for determining the amount of colloids in soils.   This paper deals chiefly with the absorptive capacities of the noncolloidal soil particles for malachite green, water, and ammonia.   The absorption of such particles is compared with the average absorptive capacities of the ultra clays extracted from different soils.   Various colloidal mineral powders and synthetic gels were also tested for absorption in order to throw light on the nature of the soil colloids.

PREVIOUS WORK.

Several investigators, including König and Hasenbäumer (14), Ogg and Hendrick (18), and Atterberg (4) have fractionated soils into various sized particles and determined the absorptive power of the different fractions for substances, such as water, dyes, gases, or salts.   The results on the whole show that the absorption by the different sized particles increases with the fineness, although not in a regular manner, and that the finer soil fractions above colloidal size absorb appreciably but much less than the colloidal material. These determinations of the noncolloidal absorption can not be accepted without question, however, since the various soil fractions were probably not entirely free from colloidal material.

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[3] The term "ultra clay" has been suggested to denote the mixture of colloidal constituents present in the soil.
[4] Details of the process are given in the paper by Moore, Fry, and Middleton (17).

Hundeshagen (*12*) and Dittler (*7*) tested, in a qualitative manner only, the absorption of various minerals for different dyes.

Ammon (*1*), and later Von Dobeneck (*8*), determined the absorptive powers of a number of finely powdered substances, including quartz, calcite, and humus for water vapor, ammonia, and other gases, and found that quartz and calcite showed a small but appreciable absorption while humus absorbed to a marked degree. Using quartz of different degrees of fineness these investigators found absorption higher in the finer fractions, but the increase due to fineness was less than the proportional increase in surface.

Stremme and Aarnio (*24*) showed that rock powders absorb but a small amount of dye and water as compared with the amount absorbed by natural clays or artificial gels. The exact fineness of the rock powders was not given, so the data throw but little light on our problem.

DISTINCTION BETWEEN COLLOID AND NONCOLLOID.

Usually colloids and noncolloids are distinguished by the size of the particles. But this distinction is not all-sufficient, especially when dealing with soil constituents, since an important part of the colloidal material in soils may be present in such a condition that it is not readily dispersable.

In the work reported here, mineral particles larger than 1 micron in diameter are assumed as noncolloids and all particles smaller than this as colloids. All the organic matter of the soil is also classed as colloid, irrespective of whether or not it happens to exist in a state of subdivision less than 1 micron. The insoluble part of more or less decomposed plant remains is of course largely made up of substances such as the celluloses, proteins, and their derivatives, which are universally classified as colloids, although in the dried state those substances may not be readily dispersable.

Certain particles, or more accurately aggregates of particles, larger than 1 micron in diameter, are also classed as colloids. These particles under the ultra microscope show no evidence of being crystalline and appear to be merely aggregates of particles which are less than 1 micron in diameter. They are presumably either difficultly reversible or irreversible colloids.

The use of 1 micron as the dividing line between colloidal and noncollodal mineral particles permits good microscopical control; since the form of particles 1 micron in size can usually be readily distinguished and such particles need not be confused with points of light emanating from very much smaller particles.

Although 1 micron is an arbitrary limit for the upper diameter of colloidal mineral particles, there is some justification for its selection, aside from mere convenience of microscopical observation. Mineral particles which are 1 micron in diameter show a distinct Brownian movement, while larger particles show practically no such activity. The international commission in 1913 decided on 2 microns as the upper limit for colloidal clay (*23*, p. 189).

OUTLINE OF INVESTIGATION.

The most obvious way of obtaining data on the relative absorptions of the colloidal and noncolloidal soil material would be to separate

the soil into two fractions, colloid and noncolloid, and then determine the absorptions of these fractions. This is similar to the method used by earlier investigators and is the one the authors first tried. The work is described under "Estimation of noncolloidal absorption from soil fractions." The data obtained in this way were not considered trustworthy, as it was exceedingly difficult to separate the bulk of the colloidal matter from the larger soil grains and it was practically impossible to tell whether or not a complete separation had been attained.

It was thought that a more accurate estimation of the noncolloidal absorption of the soil could be obtained by investigating the absorption of the individual soil minerals, since the noncolloidal part of the soil is made up of mineral particles of various degrees of fineness above the arbitrary limit of 1 micron. Each of the common soil minerals was ground to the proper fineness and the absorption of the mineral powder was determined. From the absorptive capacities of the different minerals and from the mineralogical composition of the soil, the noncolloidal absorption was calculated. Determinations by this procedure are given under "Estimation of noncolloidal absorption from mineral particles."

An indication of the nature of the colloidal material in soils was also obtained by comparing the absorptive capacities of finely ground minerals and various gels with the absorptive capacities of the mixed colloids which had actually been extracted from soils. This part of the work is detailed under "Evidence concerning the nature of the soil colloids, afforded by absorption data."

METHODS FOR DETERMINING ABSORPTION.

Determinations were made of the absorptive capacities of all samples for malachite green, water vapor, and ammonia gas. The methods followed in determining the absorption of water vapor and ammonia gas have been given in detail in previous publications and therefore need only brief descriptions.

In the absorption of ammonia (17) a sample of material which has previously been dried for 18 hours at 110° C. is exposed at 0° C. to dry ammonia gas under atmospheric pressure until absorption is virtually complete. The amount of ammonia driven off by evacuating the material at 100° C. is then determined.

The absorption of water (21) involves a determination of the amount of water which the sample will take up when exposed for five days to the vapor of 2 per cent sulphuric acid maintained at a temperature of 30° C.

The method for the absorption of malachite green, which differs somewhat from that described in a previous publication (17), is as follows: From 0.25 gram to 1 gram of material is mixed with 25 cubic centimeters of water and shaken over night. After shaking, the suspensions are treated with enough N/10 sodium oxalate solution to precipitate any soluble calcium present. The amount of sodium oxalate which it is necessary to use can be determined by a preliminary test. After adding the sodium oxalate solution, the whole is shaken 15 minutes to insure complete precipitation of the calcium oxalate. Malachite green (a 0.2 per cent solution) is then added with repeated shakings until the depth of color of the super-

natant liquid is practically the same as that of a check solution containing 10 cubic centimeters of the aforementioned dye solution in a total volume of 50 cubic centimeters. This is to insure the absorbed dye being in equilibrium with practically the same concentration of nonabsorbed dye in each determination. The suspensions are then shaken one hour in an end-over-end shaker to insure complete absorption of the dye by the soil. This time is probably longer than necessary in most cases. Sufficient normal sodium chloride solution to coagulate the colloid is then added to the suspensions; usually 5 cubic centimeters is sufficient. After a few minutes settling the suspensions are centrifuged in order to throw out any solid material and the supernatant liquid is read colorimetrically against the check solution.

ESTIMATION OF NONCOLLOIDAL ABSORPTION FROM SOIL FRACTIONS.

METHODS OF SEPARATING SOIL COLLOIDS.

In separating the colloidal matter from the larger soil grains two difficulties are encountered that are inherent in all systems of mechanical analysis: First, the difficulty of obtaining a complete deflocculation of the ultimate soil particles; second, the difficulty of sorting out the particles of different size after they have been deflocculated.

In the system of mechanical analysis heretofore practiced in the Bureau of Soils (10), treatment with a few drops of ammonia followed by long shaking have been relied on to bring about deflocculation. Williams (26) adopted long continued boiling supplemented by rubbing as the most efficient method of deflocculation. Atterberg (3) in deflocculating the soil for his system of mechanical analysis, utilizes rubbing and treatment with an alkaline solution of bromine, with hydrochloric acid and sodium hydroxide, or with concentrated nitric acid, according to the nature of the soil. König and Hasenbäumer (14) suggested boiling for a short time and repeated rubbing.

While all these methods probably deflocculate and form good suspensions of part of the colloidal matter, it is not certain that any of them deflocculates all of it. Some colloidal matter adhering to mineral particles may be difficult of separation, and we have evidence in our work that the colloidal matter which is present in the dry soil as more or less indurated aggregates is especially resistant to dispersion. In our attempts at separation we found the use of ammonia and rubbing with a rubber pestle to be especially effective. For instance, two soils when rubbed with distilled water yielded only 5 per cent and 29 per cent of colloid; but when the residues were rubbed with distilled water containing a trace of ammonia further yields of colloid, 3.5 per cent and 13.5 per cent, respectively, were obtained. Other results show the effect of rubbing. A soil that had been agitated 15 times with water containing ammonia failed to give further colloidal suspensions. However, after the pasty residue had been gently rubbed, succeeding treatments with ammonia water yielded additional amounts of colloid.

Separation of the finer particles from the coarser, after deflocculation has been produced, is brought about by subsidence in most methods of mechanical analysis. A much quicker separation, however, can be made by use of a centrifuge. In this particular investigation we made use of both subsidence and centrifuging.

PREPARATION OF SOIL FRACTIONS.

Our aim was to secure only two fractions of the soil, colloid and noncolloid; but we found the separation was facilitated in some cases by dividing the noncolloidal fraction into two groups—a coarser fraction containing the gravel and sands and a finer fraction consisting of particles ranging approximately from 0.001 to 0.050 millimeter in diameter.[5]   The colloidal fraction, as previously noted, was made up of particles less than 0.001 millimeter in diameter.

Fractions were obtained from four soils.   Details of the procedure were as follows:

Samples of 50 to 100 grams of soil were used, depending on the probable amount of colloidal matter present.   The samples were first agitated with distilled water containing ammonia (about 1 part of ammonium hydroxide to 3,000 parts H_2O).   The suspension was allowed to settle for several hours and the supernatant liquid containing the finer soil particles was then decanted and whirled for 45 minutes in a bottle centrifuge having a diameter of 22 inches and a speed of 850 revolutions per minute.   The material remaining in suspension was poured into the jar containing the colloid fraction. The residues from the centrifuge were combined with the residues left after decantation and were rubbed gently with a rubber pestle, having just enough water present to make a paste.   About a liter of water was then added and the subsidence and centrifuging repeated.   After 40 to 60 such treatments the residues yielded only the merest trace of colloid and it was evident that no more colloid was to be extracted by these methods.   The colloidal matter was concentrated to a thin paste by drawing off the water through Pasteur-Chamberland filters, using suction.   The paste of colloidal matter, as well as the coarse residues, was then air-dried.

ABSORPTION BY THE FRACTIONS.

The amounts of the different fractions separated in this manner from four soils of the humid region, together with the absorption per gram of these fractions for malachite green, water vapor, and ammonia gas are shown in Table 1.   The quantities of the different fractions obtained are expressed as percentages of the whole soil

TABLE 1.—*Absorptive capacities of different soil fractions.*

Description of soil fractions.	Part of whole soil.	Absorption per gram of material.		
		Malachite green.	Water.	Ammonia.
	Per ct.	*Gram.*	*Gram.*	*Gram.*
Huntington loam, soil:				
Colloid	10.3	0.0949	0.2221	0.0270
Fine fraction	21.9	.0288	.0476	.0098
Coarse fraction	64.0	.0114	.0215	.0062
Huntington loam, subsoil:				
Colloid	13.3	.0918	.2996	.0226
Fine fraction	19.4	.0143	.0665	.0072
Coarse fraction	63.3	.0053	.0292	.0031
Sassafras silt loam, subsoil:				
Colloid	14.4	.1398	.2732	.0293
Fine fraction	20.6	.0222	.0546	.0079
Coarse fraction	61.9	.0053	.0041	.0004
Sharkey clay, soil:				
Colloid	42.4	.3720	.3072	.0516
Fine fraction[a]	53.1	.0657	.0772	.0172

a Very little material above 0.050 millimeter present.

[5] This group corresponds approximately to the combined silt and clay groups of the Bureau of Soils classification, except that in this classification no lower limit is given for the clay (10).

It will be noted that the soil fractions containing particles from 0.001 to 0.050 millimeter in diameter had absorptive capacities averaging about 25 per cent as great as the corresponding colloids. The coarser soil fractions, made up of particles ranging mostly from about 0.050 to 2 millimeters, had absorptive values which were for the most part much lower than those of the finer fractions.

The absorptions per gram of the noncolloidal soil fractions are thus low as compared with those of the colloids. Nevertheless, if we take into account the relative amounts of the different fractions present in the soil it would appear that from 20 to 70 per cent of the total absorptive capacities of the four soils was due to the noncolloidal particles in these soils. If these data could be taken as accurately representing the absorption values of the noncolloidal part of the soil, it would be evident that the colloidal content of the soil could not be estimated with even approximate accuracy from the absorption of the whole soil.

Although the above data on the absorptive capacities of the noncolloidal soil particles are probably as good as can be obtained by this method of investigation, it is believed that they are not reliable and that they must be considerably higher than the true values. It should be borne in mind that a relatively small contamination with a highly absorptive material, such as the colloidal matter, would appreciably enhance the absorptive capacity of the noncolloidal fractions. Furthermore, we have no positive proof that the noncolloidal fractions were free from colloids. We merely know that all colloid possible was extracted with the means we employed. It is very possible that by some further treatment still more colloid could have been brought into suspension and separated, just as traces of ammonia or gentle rubbing yielded more colloid when mere agitation with distilled water was ineffective.[6]

In the process of separating the colloidal and noncolloidal portions of the soil the size of the particles in the two products was carefully checked by microscopical observation. It was evident from this control that the noncolloidal fraction was practically free from particles smaller than 1 micron in diameter and the colloidal matter contained but very few particles larger than 1 micron. However, if our methods of deflocculation were not perfect, aggregates of colloidal matter, similar to clumps of dried ferric hydroxide, or aluminum silicate gels, or partially decomposed organic matter might well have gone into the noncolloidal fraction. Examination of the dry noncolloidal fractions with the petrographic microscope indicated that this actually occurred. The fractions from the different soils which were made up of particles of 0.001 to 0.050 millimeter in diameter contained from 60 to 75 per cent of particles which could readily be identified as crystalline minerals; the rest of the material was without crystalline properties and had the same general appearance as dried inorganic gels or as the dried soil colloids, which we have separated from the soil with a supercentrifuge.

ESTIMATION OF NONCOLLOIDAL ABSORPTION FROM MINERAL PARTICLES.

Since a complete separation of colloidal from noncolloidal soil material is apparently impossible, owing to the difficulty of dis-

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[6] Williams (26) relied largely on boiling to bring about dispersion. However, boiling a fine fraction of Huntington subsoil for 18 hours failed to bring about a state of dispersion whereby all the colloid could be removed.

persing some of the colloidal material, reliable data on the non-colloidal absorption in a soil can not well be obtained from an investigation of soil fractions. It was necessary, therefore, to attack the problem in another manner.

If the noncolloidal part of the soil is made up of various mineral particles above the arbitrary limit of 1 micron in diameter, a determination of the absorptive capacities of soil minerals in the proper state of subdivision should afford data for calculating the absorption of the noncolloidal soil constituents. Data obtained in this way should be more reliable than that yielded by the preceding method of investigation, as mineral powders can be prepared which are essentially free from colloidal material.

Some 21 minerals are of common occurrence in soils. Although only a few of these are present in a soil in any considerable quantity, it was thought advisable to determine the absorptive capacity of each of them. Samples of the 21 minerals were kindly provided by the National Museum. They were characteristic mineral specimens, and were apparently free from decomposition products, although not absolutely pure, a few containing traces of calcite.

The work of previous investigators indicates that the absorptive capacity of any one mineral powder is somewhat proportional to the size of the particles,[7] and that some minerals have very low absorptive capacities. It was, therefore, advisable to test samples in a fine state of subdivision in order to obtain an accurate comparison of the absorptive capacities of different minerals. The absorptive capacities of larger particles could then be calculated closely enough for our purpose from the values of the fine particles, on the assumption that the absorptive capacity of any one kind of mineral powder is to a large degree inversely proportional to the size of the particles. Accordingly, a sample of each mineral was prepared which contained only particles ranging in size from 1 to 50 microns in diameter. This group of particles is just above the size we arbitrarily set for the colloids and corresponds to the "fine fraction" separated from the soils in the study just described.

PREPARATION OF MINERAL POWDERS.

After the minerals had been crushed to small pieces in an arbor press and in a steel mortar, they were ground either in an agate mortar or in a steel ball mill, depending on the hardness of the mineral. The harder minerals were more effectively handled in the ball mill. The samples were frequently passed through a 130-mesh sieve in order to obtain the desired fineness with a minimum amount of material finer than 1 micron. The sieved powders were then further graded by subsidence in absolute alcohol in order to remove particles that were larger than 50 microns and smaller than 1 micron in diameter. Absolute alcohol was used for the subsidence rather than water, in order to prevent the formation of colloidal matter by hydrolysis of the mineral.

The mineral powders were carefully examined under the microscope and counts made of the approximate number of particles present in the three following groups: 0.025 to 0.050 millimeter, 0.002 to 0.025 millimeter, and under 0.002 millimeter. There were but

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[7] The data of Ammon (1) and o1Von Dobeneck (8) show that while the absorption of any one mineral increases with the degree of subdivision, the increase in absorption is somewhat less than the increase in surface exposed.

very few particles larger than 0.050 millimeter or smaller than 0.001 millimeter in any of the samples. However, the different samples varied considerably in the distribution of the particles between these limits. The approximate surface exposed by 1 gram of each of the mineral powders was calculated. In this estimation account was taken of the specific gravity of the mineral; the mean diameter of each group of particles was taken as the diameter of all particles within the group, and all the particles were assumed to be spheres. No great accuracy can be claimed for these estimates of surfaces, since microscopical counts of particles of the different sizes are probably only accurate to about 10 per cent and certain of the minerals were far from spherical in shape. In the case of muscovite and biotite, the figures for surface represent only a minimum value, since the particles doubtless approximated thin plates rather than spheres. The true surfaces of these powders were probably, therefore, several times the values given in Table 2.

ABSORPTION BY THE DIFFERENT SOIL MINERALS.

In Table 2 are given the amounts of malachite green, water, and ammonia absorbed by 1 gram of each of the mineral powders and the approximate surface exposed in each case.

TABLE 2.—*Absorption of mineral particles 1 to 50 microns in diameter.*

Mineral.	Approximate surface per gram of powdered mineral.	Absorption per gram of mineral.		
		Dye.	H_2O.	NH_3.
	Square centimeter.	*Gram.*	*Gram.*	*Gram.*
[1] Apatite, $CaFCa_4(PO_4)_3$	2,813	....	0.0015	0.0000
Biotite, $K_2O.4(Mg,Fe)0.2(Al,Fe)_2O_3.6SiO.H_2O$	[2] 1,764	0.0370	.0223	.0012
[1] Calcite, $CaCO_3$	1,225	....	.0012	.0000
[3] Garnet $\begin{cases} Ca_3Al_2(SiO_4)_3 \\ Fe_3Al_2(SiO_4)_3 \end{cases}$	1,687	.0078	.0093	.0008
Chlorite, $H_8(Mg,Fe)_5Al_2Si_3O_{18}$	2,241	.0192	.0148	.0012
Cyanite, Al_2SiO_5	2,619	.0060	.0067	.0006
[3] Epidote $\begin{cases} Ca_2(AlOH)Al_2(SiO_4)_3 \, x \\ Ca_2(FeOH)Fe_2(SiO_4)_3 \, y \end{cases}$	1,131	.0001	.0016	.0008
Hornblende $\begin{cases} Ca(Mg,Fe)_2(SiO_3)_3 \\ Na_2Al_2(SiO_3)_4 \\ (Mg,Fe_4)(AlFe_2)SiO_4 \end{cases}$	1,165	.0089	.0018	.0000
Limonite, $Fe_2(OH)_6Fe_2O_3$	753	.0053	.0308	.0052
[4] Magnetite, Fe_3O_4	674	....	.0006	.0000
Microcline, $KAlSi_3O_8$	3,104	.0001	.0008	.0000
Muscovite, $K_2O.3Al_2O_3.6SiO_2.2H_2O$	[2] 2,025	.0390	.0509	.0023
Orthoclase, $KAlSi_3O_8$	3,449	.0005	.0016	.0000
Plagioclase $\begin{cases} NaAlSi_3O_8 \, x \\ CaAl_2Si_2O_8 \, y \end{cases}$	3,229	.0000	.0028	.0000
Quartz, SiO_2	3,179	.0000	.0005	.0002
Rutile, TiO_2	694	.0000	.0240	.0012
Sillmanite, Al_2SiO_5	1,609	.0105	.0022	.0008
[3] Titanite, $CaO.TiO_2.SiO_2$	2,694	.0059	.0039	.0010
Tourmaline, $Na_2O,(Fe,Mg,Cr)O,Al_2O_3,SiO_2,B_4C_3H_2O$	1,386	.0130	.0007	.0000
Zircon, $ZrSiO_4$	977	.0048	.0055	.0012
[3] Zoisite $\begin{cases} Ca_2(AlOH)Al_3(SiO_4)_3 \, x \\ Ca_2(FeOH)Fe_2(SiO_4)_3 \, y \end{cases}$	1,166	.0000	.0078	.0007
Average values	1,885	.0088	.0095	.0008

[1] Calcite, and probably apatite, in the absence of colloidal soil material develops an alkaline reaction in the process of the dye determination, and thus decolorizes the malachite green oxalate. This decolorization, however, does not take place when soil material is present to act as a buffer.
[2] Owing to plate-like form of particles, this represents minimum surface.
[3] Trace of calcite present which was removed by 4 per cent HCl before making the dye determination.
[4] Trace of calcite present.

Ammonia gas was not absorbed at all by eight minerals and appreciable amounts were absorbed by only two, muscovite and limonite. Malachite green was absorbed in considerable amounts by muscovite, biotite, and chlorite, and to a lesser degree by tourmaline and several others. Four of the commonest soil minerals, on the other hand, did not absorb a measurable amount of the dye. Water vapor was absorbed by all minerals, although significant amounts were absorbed by only five. The minerals which are usually present in soils in the greatest amount—quartz and the feldspars—showed practically no absorption for the dye, water, or ammonia.

There appeared to be no correspondence between the amounts of malachite green, water, or ammonia absorbed by the different minerals. Rutile, for instance, was highly absorptive of water but not of malachite green or ammonia. On the other hand, tourmaline had a considerable absorption for malachite green, only a very slight absorption for water, and no absorption for ammonia. Limonite, which shows especially high absorption for water and ammonia, is usually considered as being a colloidal mineral. These results agree with Greenland's (11) conclusion that crystalline minerals as well as the gel minerals may show some absorption.

While there is of course some proportionality between the outer surface exposed by any one mineral and its absorptive capacity, that is the finer any particular mineral is the more it will absorb, it is apparent from the above table that the absorptive capacities of the different minerals were not proportional to the outer surfaces exposed. Each mineral seems to have a characteristic absorptive capacity for the different substances.

ABSORPTION BY THE MINERAL PARTICLES IN THE SOIL.

With determinations available of the absorptive values of practically all the important unaltered minerals found in normal soils, it is possible to make an approximate evaluation of the part such minerals have in the total absorption of a soil, provided the mineral composition is known.[8] Thus, it is possible to calculate what is probably the truly noncolloidal absorption of the fractions described under "Estimation of noncolloidal absorption from soil fractions." With this in view, a quantitative mineralogical examination was made of the "fine fraction" in each of the soils. The results were as follows:

Huntington loam, soil, fine fraction, 50 per cent quartz, 2 per cent other crystalline minerals, and 48 per cent indeterminate colloid-like material.

Huntington loam, subsoil, fine fraction, 75 per cent quartz, trace of other crystalline minerals, 25 per cent indeterminate colloid-like material.

Sassafras silt loam, subsoil, fine fraction, 60 per cent quartz, 1 per cent muscovite, 1 per cent other minerals, 38 per cent indeterminate colloid-like material.

Sharkey clay loam, soil, fine fraction, 50 per cent quartz, 5 per cent muscovite, 3 per cent other crystalline minerals, 42 per cent indeterminate colloid-like material.

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[8] While optical methods are not applicable for the identification of minerals below 0.005 millimeter in diameter, crystalline outline can usually be distinguished in material down to about 0.001 millimeter.

Table 3 shows, for the four soils studied, that part of the total absorption of the soil which must have been due to the unaltered minerals present. In compiling this table the absorption of each fine fraction was calculated from the mineralogical composition given above and from the absorption data for particles of this size given in Table 2. The absorption of each coarse fraction was calculated from that of the corresponding fine one, assuming that the two fractions were of the same mineralogical composition and that the absorptive values were therefore inversely proportional to the size of the particles.

TABLE 3.—*Part of soil absorption due to unaltered minerals.*

Type of soil.	Absorption of the unaltered minerals present in 1 gram of soil.			Absorption of 1 gram of soil.[1]			Part of soil absorption due to unaltered minerals, in case of—		
	Malachite green.	H₂O.	NH₃.	Malachite green.	H₂O.	NH₃.	Malachite green.	H₂O.	NH₃.
Huntington loam, soil..............	*Gram.* 0.0002	*Gram.* 0.0002	*Gram.* Trace.	*Gram.* 0.0234	*Gram.* 0.0508	*Gram.* 0.0089	*Per cent.* 0.8	*Per cent.* 0.4	*Per cent.* Trace.
Huntington loam, subsoil...........	Trace.	Trace.	Trace.	.0193	.0712	.0064	Trace.	Trace.	Trace.
Sassafras silt loam, subsoil...........	.0005	.0006	Trace.	.0286	.0530	.0060	1.7	1.1	Trace.
Sharkey clay, soil...	.0007	.0009	Trace.	.1880	.1712	.0312	.4	.5	Trace.

[1] Calculated from the absorption given for fractions in Table 1.

It is evident from Table 3 that the absorption of the noncolloidal minerals is less than 2 per cent of the total soil absorption in each of the four soils described and is therefore negligible as compared with the absorption of the colloid. This value for the noncolloidal absorption is very much lower than that shown by the first method of investigation and is, we believe, much more accurate.

The preceding calculations show the relative absorptions of the colloids and noncolloids in four soils only, but a rough estimate can be made for soils in general. The average absorptions per gram of the unaltered common soil minerals of silt and clay size for malachite green, water, and ammonia, as shown in Table 2, are, respectively, 0.0088, 0.0095, and 0.0008, while the averages for ultra clays extracted from some 40 different soils are respectively 0.200, 0.298, and 0.040.[9] The average absorptions per gram of unaltered minerals just above the colloidal size are thus only 4 per cent, 3 per cent, and 2 per cent as high as those of the colloids for malachite green, water, and ammonia.

Since there are such wide variations in the absorptions of the different minerals, a proper estimate can not be made of the relative absorptions of the colloidal and noncolloidal parts of the soil unless consideration is given to the relative quantities in which the different minerals are present. In a former bulletin of the Bureau of Soils (19) mineralogical analyses are given of the finer sand and silt groups in 26 representative American soils. The average mineralogical composition of the silt group in these 26 soils is as follows: Quartz 51 per

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[9] The extreme variations in the absorptions per gram of the different ultra clays are: 0.431 and 0.070 gram of malachite green, 0.348 and 0.240 gram of water, and 0.076 and 0.019 gram of ammonia.

cent, potash feldspars 7 per cent, muscovite 7 per cent. Miscellaneous minerals, no one of which is present in important amount, together with colloidal aggregates, make up the remaining 35 per cent of the group.[10] The quartz and feldspar mineral powders reported in Table 2 had no appreciable absorption for malachite green, water, or ammonia. It is therefore evident that on an average at least 68 per cent of the mineral particles which are from 1 to 50 microns in size would have practically no absorption. (This is assuming that the minerals in the clay group are essentially the same as those in the silt group.) If we take the average absorption of the other mineral powders as representing the absorption of the remaining 32 per cent of silt and clay particles, the average absorptions per gram of the unaltered minerals in the soil just above the colloidal size would be only 1.7 per cent, 1.1 per cent, and 0.8 per cent that of the average absorption of the ultra clays for malachite green, water, and ammonia, respectively.

In the mechanical groups larger than silt, somewhat over 68 per cent of the mineral particles would probably be quartz and feldspars, since quartz is more abundant in the larger soil separates. Hence in calculating the absorption of mineral particles in the fractions larger than silt, it will be safer to assume that so far as their mineralogical composition is concerned their absorption will be less than that of particles of silt size.

Particles of different sizes of any one crystalline mineral must have absorptive capacities that are to some degree inversely proportional to the size of the particles. On this basis the absorptive capacities of particles from 2 to .25 millimeters in diameter, included in the gravel, coarse sand, and medium sand groups, would be only about one-fortieth as great as that of particles of silt and clay size, and may, therefore, be disregarded. On the same basis, the finer mineral sands, with diameters from 0.05 to 0.25 millimeters would have absorptive capacities one-sixth that of particles of the silt and clay size.

The application of the above facts to a few hypothetical soils will make evident what part the noncolloidal soil particles may be expected to play in the absorption of different types of soils.

Let us assume a loam soil of about average mineral content made up of 45 per cent quartz, 5 per cent muscovite, 5 per cent feldspars, 15 per cent other crystalline minerals, and 30 per cent of colloid. The maximum amount of particles under 0.05 millimeter for a loam soil, according to the classification used in the Bureau of Soils, is 60 per cent. We should then have 60 per cent of material smaller than 0.05 millimeter and 40 per cent larger than 0.05 millimeter. The average size of the latter may well be taken at 0.5 millimeter. If we assume average absorptions for the colloidal matter and calculate the mineral values from Table 2, we should have a gram of the soil absorbing 0.0618 gram dye, 0.0914 gram water, and 0.0121 gram ammonia. The percentages of these total absorptions which were due to the minerals would be respectively 2.9 per cent, 2.2 per cent and 1 per cent. Most of the mineral absorption in this case would be due to mica.

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[10] Recent work has shown that 15 per cent or more of the silt group may consist of colloidal aggregates when this group is separated by the method of mechanical analysis practiced in the Bureau of Soils. Assuming 15 per cent of colloidal aggregates in this group, the average composition of the crystalline minerals would be: Quartz 60 per cent, potash feldspars 8 per cent, muscovite 8 per cent, and miscellaneous minerals 24 per cent.

Although the mineral content assumed in this case is about the average of a large number of soils, most soils do not contain this amount of muscovite. The mica average of 5 per cent is due to the very high mica content of a few important soil types. Usually the muscovite content is below 2 per cent. If the hypothetical soil just considered had contained 2 per cent of muscovite, only approximately 1 per cent of the total absorption would have been due to the crystalline minerals. If, however, the muscovite content had been as high as 37 per cent, which has been reported for one of our most highly micaceous soils, the mineral absorption values might have been as high as 7 to 20 per cent of the total soil absorption, the dye absorption being most affected by the mica.

In the case of a peat soil, the total mineral matter is small in amount, so the absorption of the minerals would be negligible. The organic matter, as indicated before, may be considered essentially colloidal.

EVIDENCE CONCERNING THE NATURE OF SOIL COLLOIDS AFFORDED BY ABSORPTION DATA.

It is difficult to understand why so small a part of the absorptive capacity of the whole soil should reside in the noncolloidal constituents unless the colloidal constituents differ from the noncolloidal in other respects than mere degree of subdivision. The organic matter of soils, which is classified as colloidal, is obviously of a different nature from the mineral particles; but in many soils organic matter forms only a small part of the total colloidal content. Other investigations in this bureau indicate that the larger part of the inorganic colloidal matter in soils is different from the noncolloidal mineral particles in being similar to gels. This view that the soil colloids are mostly of a gel-like nature is also held by Van Bemmelen (5), Rohland (22), König (13), Ehrenberg (9), Wiegner (25), and others.

The fact that the mineral powders just above the colloidal size had such low absorptions as compared with the ultra clays is in harmony with the view that the two classes of material are of a different nature. However, since most of the colloidal particles are so small that their size can not be accurately determined microscopically, the possibilities would still remain, so far as microscopical observation is concerned, that the colloidal and noncolloidal parts of the soil are of the same nature and that the differences in absorptian are merely a function of the size of the particles, the colloidal particles being exceedingly fine as compared with the noncolloidal particles.

It therefore became desirable to determine the absorptions of mineral powders ground as finely as possible and to compare the absorptions of these powders with those of the coarser powders and ultra clays.

ABSORPTIVE CAPACITIES OF MINERAL PARTICLES BELOW 1 MICRON IN DIAMETER.

Six minerals which showed but little tendency to flocculate when suspended in water were selected for grinding to colloidal dimensions. The minerals were ground dry in a steel ball mill—muscovite for 10 days and the other minerals for about 3 days. The powders from the ball mill were then shaken with distilled water and the greater part

of the colloidal particles separated from the particles above 1 micron in diameter by means of the centrifuge. This procedure was the same as that followed in separating colloids from soils, except that no ammonia was used with the mineral powders.

Determinations of the absorptive capacities of each of the powdered minerals for malachite green, water, and ammonia are given in Table 4.

TABLE 4.—*Absorption of mineral particles less than 1 micron in diameter.*

Mineral powder.	Absorption per gram of mineral powder.		
	Mala-chite green.	H_2O.	NH_3.
	Gram.	Gram.	Gram.
Muscovite	0.0829	0.3581	0.0141
Limonite	.0078	.2289	.0100
Chlorite	.1168	....	.0091
Microcline	.0000	.1694	.0067
Orthoclase	.0242	.1673	.0077
Quartz	.0000	.0870	.0049
Average	.0386	.2021	.0088

The absorptive powers of these very fine mineral powders for malachite green present striking contrasts. Microcline and quartz did not absorb a detectable amount of dye. On the other hand, chlorite and muscovite had absorptive capacities which were as high as the least absorptive ultra clays found in 33 different soils. In no case was the absorption as high as the average for soil colloids.

The different minerals varied less in their absorptive capacities for water vapor. The values for muscovite and limonite are not greatly different from the average for soil colloids; the others, however, are somewhat lower.

None of the mineral colloids absorbed as much ammonia as the least absorptive ultra clay we have tested, and the average value for the mineral powders is only 22 per cent of the average value for the ultra clays.

While the absorptive capacities of these mineral powders were, on the whole, much greater than those of the 1 to 50 micron powders, they were much lower than those of the ultra clays, particularly as regards absorption of the dye.

The absorptive values obtained for these minerals doubtless did not represent accurately the true absorptive capacities of *unaltered* minerals of any particular size. In preparing these fine powders it was necessary to treat the material with 2 to 10 liters of distilled water for each gram of colloidal mineral extracted, in order to remove completely the coarser particles, and the material was in contact with water for three to five days. There was, therefore, opportunity for considerable alteration or breaking down of the minerals through hydrolysis. Hence, a considerable part of the absorptive capacities of these preparations may well have been due to the presence of colloidal decomposition products of the minerals.

It is well recognized that many silicate minerals are acted upon by distilled water, yielding an alkaline solution and doubtless insolu-

ble hydrolytic products of colloidal nature. This action of course becomes more pronounced the finer the particles. Cushman (6) shows that this action takes place to an appreciable extent in a few hours and suggests that a colloidal film is thereby formed on the surface of the particles. Michaelis (15) states that some finely powdered quartz which he prepared absorbed water and swelled; also that a silicic acid gel may be made by boiling a quartz suspension for several days. We found that treating powdered orthoclase with hot water for two days, then leaching free from soluble salts, increased its absorptive capacity for water vapor from 0.0016 gram to 0.0046 gram.

The fact that the most finely powdered minerals, even though they must have suffered considerable alteration, had absorptive capacities less than the ultra clays, affords some evidence that the colloidal matter in soils is not made up of merely finely divided minerals. More conclusive evidence of this, however, is afforded by analytical data which are being prepared for publication. These data show that no probable combination of soil minerals has the same chemical composition as the typical colloidal matter in soils.

ABSORPTIVE CAPACITIES OF SYNTHETIC GELS.

It was thought that further evidence on the nature of the colloidal matter in soils might be obtained from the absorptive capacities of inorganic gels; since, as previously stated, other investigations in this bureau indicate that the colloidal material in soils is largely of a gel-like nature. An examination of the ultra clays extracted from many different soils has indicated that they consist chiefly of aluminum silicate with some ferric silicate and one or more of the following substances in the gel form: ferric hydroxide, aluminum hydroxide, organic matter, and possibly silicic acid (20). If this is true, it would seem that synthetic preparations of these individual gels should have absorptive capacities of the same order as the ultra clays. Four of these gels were therefore prepared and their absorptions tested.

An aluminum silicate gel was made from sodium silicate and aluminum chloride mixed in the proper proportions for forming kaolinite ($Al_2O_3 . 2SiO_2 . 2H_2O$); the ferric hydroxide was prepared from ferric chloride and sodium hydroxide; the aluminum hydroxide from aluminum chloride and sodium hydroxide; and the silicic acid from sodium silicate and sulphuric acid. The gels thus formed were repeatedly washed with large amounts of distilled water until practically free from soluble salts. The wash waters were removed through Pasteur-Chamberland filters, using suction, and the gels, after being concentrated by air-drying, were ground to pass a 200-mesh sieve.

For comparison with these freshly prepared gels, a sample of silica gel was procured from a commercial chemical company and samples of alumina and iron gels from the Chemical Warfare Service. The absorptive capacities of these products all ground to pass a 200-mesh sieve are shown in Table 5. Included in this table also are the absorptions of a peat soil and of an extract from it containing no particles above 1 micron. The peat soil contained very little mineral matter, so these samples are probably fairly representative of the organic colloids in soils.

TABLE 5.—*Absorption of gels.*

Description of sample.	Absorption per gram of gel.		
	Malachite green.	H_2O.	NH_3.
	Gram.	Gram.	Gram.
Silica gel:			
Freshly prepared	0.0348	0.8658	0.1426
Commercial product	.0080	.2015	.0966
Aluminum hydrate gel:			
Freshly prepared	.0689	.6155	.0525
Chemical Warfare Service product	.0735	.3500	.0596
Ferric hydrate gel:			
Freshly prepared	.0920	.3090	.0293
Chemical Warfare Service product	.1160	.3106	.0478
Aluminum silicate gel, freshly prepared	.5334	1.0888	.0504
Peat	.2736	.2907	.1274
Peat, particles below 1 micron	.0982	.2990	.0563
Average values	.1443	.4812	.0736

The different gels, just as the mineral powders, varied widely in their absorptive capacities for malachite green, water, and ammonia. It is significant that on the whole the absorptions of the gels were much greater than those of minerals ground below 1 micron, and were in a class with those of the ultra clays. The average absorption of all the gels was somewhat below that of the ultra-clay average for malachite green, but higher for water and ammonia.

A close agreement between the average absorptions of the gels and ultra clays is, of course, not to be expected, since the ultra clays would not be composed of equal amounts of each of these gels. Moreover, the absorptive capacities of synthetic gels vary greatly, according to what appear slight differences in methods of preparation, and they are also profoundly affected by changes generally described as aging. Differences between the absorptive capacities of our gels and those of the chemical company and the Chemical Warfare Service are doubtless due to differences in both method of preparation and age of product.

The absorptive data on colloidal mineral powders and synthetic gels are, on the whole, in harmony with the view that the larger part of the colloidal material in soils is not made up of mineral particles but of substances in a gel-like condition. In itself the absorptive data is not conclusive evidence, but it is confirmatory of similar conclusions arrived at in other investigations.

GENERAL DISCUSSION.

The data accumulated in this work indicate that, as a rule, considerably less than 5 per cent of the absorptive capacity of a soil is located in the unaltered mineral particles and that 95 per cent or more of the absorption is due to the colloidal material. It is realized that this distribution of the absorptive capacity of a soil, which was determined for malachite green, water, and ammonia gas, might not hold for all substances, although these three substances differ widely in their chemical and physical properties.

If 95 per cent or more of the absorption of the whole soil is due to the colloidal constituents, the accuracy of absorptive methods for

determining the colloidal content of a soil obviously would not be affected appreciably by the noncolloidal constituents. One of the fundamental objections against absorptive methods of estimating the colloids is thus removed. It is not intended to imply, however, that even relative colloidal contents of different soils are indicated by the mere absorptive capacities of the soils for such substances as malachite green or ammonia; since the colloids from different soils absorb widely varying amounts of these substances.

The almost complete localization of absorption in the colloidal matter probably is due primarily to the colloidal material being of a quite different nature from the larger soil particles. While the noncolloidal part of the soil is made up of unaltered soil minerals, the colloidal material is doubtless made up chiefly of inorganic gels, the insoluble decomposition product of soil minerals, together with amorphous organic matter.

The results on the noncolloidal absorption of soils are evidently at variance with some of the older, but still prevalent, concepts regarding soil absorption. It has been generally recognized that the organic matter constitutes an especially absorptive part of the soil, and the old view was that the rest of the absorption was due to mineral particles of all degrees of fineness, the finer the particles the more absorptive the soil. Absorption was thus regarded as proportional to the surface exposed, and the surface, except for the organic matter, was considered as being almost entirely that of mineral particles. The more highly absorptive soils were supposed to contain some especially absorptive minerals called zeolites. It is now well recognized that zeolites, if present at all in soils, can be there only in very small amounts.

It is now coming to be realized that the highly absorptive inorganic material in soils is not the definite crystalline zeolites, but amorphous material such as ferric hydroxide, aluminum hydroxide, silicic acid, and aluminum silicate gels. The data here presented tend to confirm the more modern view of soil absorption, and gives for the first time a quantitative estimate of the amount of absorption due to the colloidal material and the amount due to the noncolloidal particles.

SUMMARY.

It was impossible to determine directly the amount of absorption in soils due to colloids and noncolloids from a fractionation of the soil into these two classes of material, since we could not separate all the colloidal matter from the finer mineral particles.

Since the noncolloidal part of soils is made up of minerals of different degrees of fineness, it should be possible to calculate the magnitude of the noncolloidal absorption in the soil from the absorptive capacities of minerals powdered to definite sizes.

Each mineral has a characteristic absorptive capacity for different substances. Several of the most abundant minerals in soils, such as quartz and the feldspars, absorb practically no malachite green, water or ammonia.

It was calculated from the absorption of mineral powders and the mineralogical compositions of soils that as a rule less than 5 per cent of the total absorption of the soil is due to the noncolloidal part. In the case of the most highly micaceous soils, however, the

noncolloidal absorption might reach 10 to 20 per cent of the whole soil absorption.

Absorption by noncolloidal constituents should, therefore, not seriously affect absorptive methods for determining the amount of colloids in soils.

Evidence concerning the nature of the soil colloids is afforded by the absorptive capacities of various substances. Minerals ground to a state of subdivision probably equal to that of the mixed soil colloids, or "ultra clays," absorbed less than the average ultra clay. The average absorption of peat and synthetic inorganic gels, on the other hand, was more nearly like that of the ultra clays.

Since soil colloids appear to be of quite a different nature from the noncolloidal particles, and not merely finely comminuted minerals, it is understandable why such a large part of the absorption of a soil should be localized in the colloidal matter.

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